EFFECTS OF SURFACE-ACTIVE AGENTS ON MOLYBDENUM ADSORPTION ONTO COAL FOR LIQUEFACTION

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INTRODUCTION

The aim of this work is to enhance catalyst loading and dispersion in coal for improved liquefaction by preadsorption of surfactants onto coal. The use of surfactants to increase the dispersion and stability of coal-water slurries and to enhance coal beneficiation is well known. However, the effects of surfactants on catalyst loading and dispersion prior to coal liquefaction have not been investigated. This paper discusses the influence of the cationic surfactant dodecyl dimethyl ethyl ammonium bromide (DDAB) and sodium dodecyl sulfate (SDS, anionic) on the surface properties of Illinois No. 6 coal and its molybdenum uptake from solution.

Extensive investigations on molybdenum and other metals as coal liquefaction catalyst precursors have shown that more effective catalyst loading techniques are required to attain sufficiently high levels of catalyst dispersion in coal for liquefaction on a commercial scale. Studies (1-3) in our laboratory have shown that the surface charge properties of coal exert significant influence on the uptake, dispersion and activities of aqueous soluble calcium and potassium catalysts that were applied to coal char gasification. In general, the surfaces of the three types of coal investigated were negatively charged. The surface charge density was linked to the dissociation of coal surface phenolic and carboxylic groups which promoted the adsorption and dispersion of calcium and potassium ions (1, 2).

Coal surface contains both hydrophobic and hydrophilic sites. The hydrophilic regions consist of inorganic or polar organic surface groups; the hydrophobic surface regions are primarily non-polar organic moieties. When added from aqueous solution, the catalyst will be attracted to the hydrophilic sites on the coal but it will be repelled by the hydrophobic sites. The opposite effect will occur when a catalyst is loaded from organic solution. In either case, a low catalyst dispersion will result, unless the coal surface sites are controlled to optimize the distribution of the catalyst in the coal. The current work examines the application of surface-active agents (surfactants) for controlling coal surface properties with the goal of enhancing molybdenum loading and dispersion prior to liquefaction.

EXPERIMENTAL

The Illinois No.6 coal (DECS-24) used in this study was supplied by the Penn State Coal Sample Bank. Its moisture, ash, volatile matter, and fixed carbon contents were 13.2, 11.6, 35.4, and 39.7 %wt., respectively, on as-received basis. It has an ultimate analysis of 11.6 % ash, 57.3% carbon, 4.0% hydrogen, 1.0% nitrogen, 4.8% sulfur, and 8.1%wt. oxygen (by difference). Coal-water slurries for the study were prepared by adding 2.0g of coal to 25 mL of 0.01M aqueous solution of molybdenum and 25 mL of 0.02M DDAB or 0.02M SDS. A set of six samples were

prepared for each surfactant and the pHs of the slurries ranged from about 2 to 12. Ammonium molybdate (VI) tetrahydrate (AMT) was used as the molybdenum source. After recording the original pHs of the coal dispersions, about 0.5mL of 1M HCl or 0.5M NaOH solution was added to all, except one sample, to adjust the pHs to the desired values. The samples were then shaken on a mechanical agitator for 24h, followed by redetermination of the final equilibrium pHs. The samples were then filtered and the filtrates were analyzed for molybdenum using atomic absorption spectrophotometry. The molybdenum content of the coal residues was measured by Galbraith Laboratories, Knoxville, TN, using inductively coupled argon plasma spectroscopy. Mass balance calculations showed good agreement between the two analytical techniques.

To determine the effects of the coal surface charge on the adsorption of the surfactants and molybdenum, the zeta potentials of coal slurries containing 5g of coal per liter and deionized water were measured. The measurements were conducted on 25 mL samples to which 25 mL of 0.2M, 0.02M, or 0.002M DDAB or SDS solution had been·added and the pHs adjusted as described above. The samples were equilibrated for 4h by mechanical agitation, after which the pH values were recorded. The zeta potentials were measured at room temperature using a Pen Kem Model 501 zeta meter.

The interaction of the surfactants with the coal surface was studied using diffuse reflectance FTIR. The coal samples were dispersed in infrared grade KBr that had been dried overnight at 300°C and sieved through a 90 micron sieve. The FTIR spectra were recorded on 10% coal in KBr using a Nicolet Magna IR Spec 750 and 500 scans.

RESULTS AND DISCUSSION

The zeta potential results in Figure 1 show that the parent coal is negatively charged within the pH range investigated and that the charge density increased with increase in the slurry pH. This behavior is attributed to the dissociation of the surface carboxlylic and phenolic acid groups (1, 2). Figure 1 also shows that the coal particles generally produced positive zeta potentials in the presence of DDAB. In solution, SDS ($CH_3(CH_2)_{11}OSO_3^-Na^+$) and DDAB ($CH_3(CH_2)_{11}N(C_2H_5)(CH_3)_2^+Br^-$) will dissociate to produce anionic and cationic surfactants, respectively, which can be denoted as $ROSO_3^-$ and $R'N^+$. Since DDAB is cationic, the positive charge density on the coal can be explained by the coulombic attraction of the surfactant, and its subsequent adsorption, to the negatively charged sites on the coal surface. In contrast to the effect of DDAB, the zeta potentials of the coal particles became more negative than those of the parent coal in the presence of SDS, as shown in Figure 2. The negative charge density increased with increase in pH and in the concentration of SDS. Since the surface of the raw coal is negative, the adsorption of SDS must occur through the hydrocarbon chain of the molecule, with the anionic head oriented towards the aqueous solution.

The effects of the surfactants and pH on molybdenum loading onto the coal are shown in Figure 3. A remarkable dependence of catalyst loading on both parameters was observed. The minimum catalyst loading occurred on the parent, untreated coal in contrast to the DDAB-treated coal which contained the highest molybdenum content. Around pH 2.5, the molybdenum loadings of these samples were about 5 and 15

mg/g of coal, respectively. An intermediate molybdenum loading (~9 mg/g coal) occurred on the SDS-treated sample.

The observed molybdenum adsorption patterns can be explained by the electronic charges on the coal surface and on the molybdenum species. In aqueous solution, AMT will dissociate to form various molybdenum oxyanions which are pH dependent (4). It is reported that $Mo_8O_{26}^{4-}$ predominates below pH 2 whereas $Mo_7O_{24}^{6-}$ exists as the dominant species between pH 2 and 6. MoO_4^{2-} and $Mo_7O_{24}^{6-}$ occur in the pH 6 to 8 range; MoO_4^{2-} predominates above pH 8. Thus, the adsorption of the molybdenum species should be promoted by the positively charged DDAB sites on the coal. It is observed from Figure 1 that at 10^{-3} M DDAB, the zeta potentials are positive and become negative above ~pH 9. At 10^{-2} M DDAB, the zeta potentials are positive within the entire range of pH studied and they increased almost exponentially with increase in pH. This implies progressively stronger adsorption of DDAB onto the coal surface. When the DDAB concentration was raised to 10^{-1} M, the zeta potential increased steadily, passed through a maximum around pH 6-8, and then decreased thereafter. This phenomenon is attributed to strong DDAB adsorption and micelle formation. When the DDAB concentration on the surface exceeded the critical micelle concentration around pH 6-8, the molecules formed aggregates with the polar head of the surfactant oriented towards the interior of the micelle (5). This should decrease the positive charge density on the coal, as was indicated by the decline in the zeta potential values.

The FTIR spectra of the original, untreated coal and those onto which molybdenum and DDAB or SDS were adsorbed are shown in Figure 4. The FTIR spectrum for the original coal after loading with molybdenum is provided in Figure 4A. Significant differences can be seen in the C-H bands at 2800-3000 cm^{-1}. The intensities of these bands are higher for the surfactant-treated samples than for the raw coal (Figure 4B). It is also noted that the intensity of the DDAB-treated coal (Figure 4C) is stronger than for the SDS-treated specimen (Figure 4D). The FTIR spectra confirmed the adsorption of the surfactants onto the coal surface.

In conclusion, it has been shown that the adsorption of molybdenum onto Illinois No. 6 coal (DECS-24) is significantly promoted by preadsorption of dodecyl dimethyl ammonium bromide (DDAB) and sodium dodecyl sulfate (SDS). The former surfactant effected higher catalyst loading since its cationic character favored its adsorption onto the negatively charged coal surface and promoted the uptake of molybdenum oxyanions. This study has shown that the surface properties of coal can be modified for effective catalyst loading onto coal. The influence of the catalyst addition technique on catalyst dispersion and on coal liquefaction activities will be discussed in subsequent papers.

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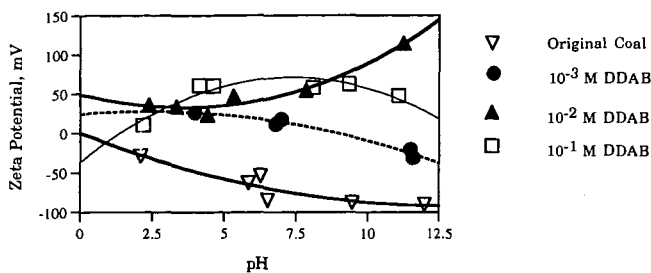
Figure 1.   Zeta Potential of DECS-24 Coal as a
            Function of DDAB Concentration and pH.
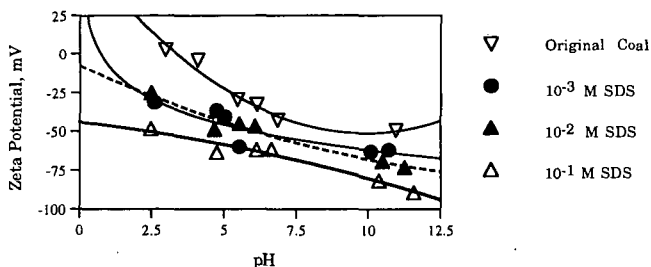

Figure 2.   Zeta Potential of the Coal as
            a Function of SDS Concentration and pH.
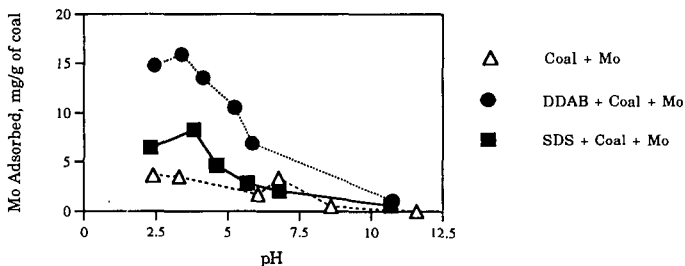

Figure 3.   Effect of Surfactant and pH on Molybdenum
            Adsorption by the Coal.

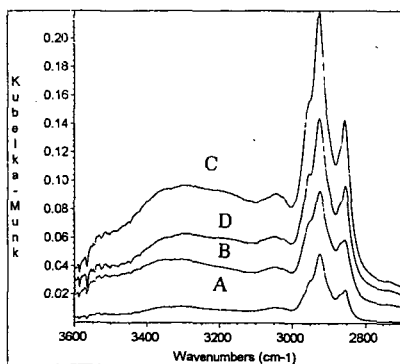
Figure 4.   FTIR spectra of the Original and the
            Surfactant-Treated Coals after
            Molybdenum Adsorption.
            A: Coal + Mo; B: Original Coal only;
            C: Coal + DDAB + Mo; D: Coal + SDS + Mo